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Searching for switchable molecular conductors: Salts of $[M(dcbdt)_2]$ (M = Ni, Au) anions with $[Fe(sal_2\text{-trien})]^+$ and $[Fe(phen)_3]^{2+}$

L.C.J. Pereira, A.M. Gulamhussen, J.C. Dias, I.C. Santos, M. Almeida *

Departamento de Química, ITN/CFMCUL, E.N. 10, P-2686-953 Sacavém, Portugal

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Abstract

Salts of $[Fe^{III}(sal_2\text{-trien})]^+$and $[Fe^{II}(phen)_3]^{2+}$ cations and $M[(dcbdt)_2]^-$ anions with M = Ni and Au (dcbdt = dicyanobenzenedithiolate) with formula $[Fe(sal_2\text{-trien})][M(dcbdt)_2]$ and $[Fe(phen)_3][M(dcbdt)_2]_2$ were obtained and characterized by single X-ray diffraction and magnetic measurements. None of these salts shows a clear spin crossover behaviour and their magnetic properties are due essentially to the cations in a high spin S = 5/2 and low spin states for the Fe^{III} and Fe^{II} salts respectively. The magnetic Ni sublattices in both compounds appear to have a negligible direct contribution to the magnetization but enhance the AF interactions in the cation sublattice.

Keywords: Fe complexes; Magnetic properties

1. Introduction

Recently there has been an increasing interest in achieving molecular conducting systems in which the electrical conducting properties can be modulated by variations in the spin state of spin cross-over units incorporated in such a solid. Using a hybrid molecular approach such type of materials could be achieved in a salt, by combination of a spin crossover system, with appropriated molecules which in the solid state may form electrically conducting partially oxidized extended networks.

Since the spin crossover compounds known so far are essentially cationic complexes, mainly of Fe^{II} or Fe^{III} [1], this hybrid approach implies that the conducting network is based on anionic species. Indeed in an attempt to achieve hybrid conducting materials some Fe spin crossover cations such as $[Fe(sal_2\text{-trien})]^+$ (sal_2-trien is the ligand obtained from the condensation of two molecules of salicylaldehyde and triethylamine) have been recently combined with anionic $[M(dmit)_2]^{n-}$ complexes (dmit = 1,3-dithiole-2-thione-4,5-dithiolate) [2,3]. The $[M(dmit)_2]$ complexes are well known as capable of forming in the solid state partially oxidized extended networks which are at the base of several molecular metals and even superconductors [4]. However, the compounds obtained so far with $[M(dmit)_2]$ anions are at most semiconductors with modest electrical conductivity, and in some cases the spin transitions are absent.

In this context it is important to explore new compounds with spin crossover cations and other molecules capable of making anionic conducting networks. We have previously described another type of anionic transition metal bisdithiolene complexes, $[M(dcbdt)_2]$ (dcbdt = dicyanobenzenedithiolate) which can exist in a variety of oxidation states [5], including partially oxidised ones associated with high electrical conductivity, such as in $[n\text{-}Bu_4N]_2[M(dcbdt)_2]_5$ M = Ni, Au [6]. In this paper we describe new charge transfer salts of $[M(dcbdt)_2]$ anions with M = Au and Ni with the Fe^{III} and Fe^{II} cations $[Fe(sal_2\text{-trien})]^+$ and $[Fe(phen)_3]^{2+}$ (see Scheme 1).

* Corresponding author. Tel.: +351 219946171; fax: +351 2199414155.
E-mail address: malmeida@itn.pt (M. Almeida).

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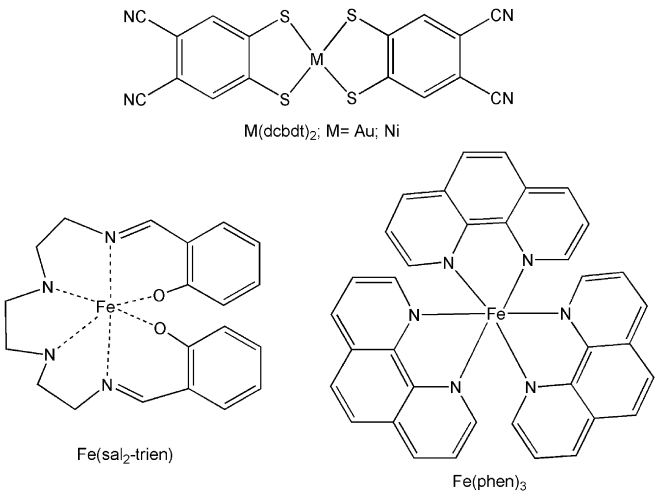

Scheme 1.

2. Experimental

2.1. Synthesis

The salts (n-Bu_4N) [Ni(dcbdt)$_2$] and (n-Bu_4N) [Au(dcbdt)$_2$] were prepared by using the procedures previously reported [5]. The salts [Fe(sal$_2$-trien)] (PF_6) and [Fe(Phen)$_3$] (PF_6)$_2$ were prepared as described in the literature by Tweedle and Wilson [7] and Decurtins et al. [8]. All solvents were dried under nitrogen prior to use. Elemental analyses were performed by the analytical services of ITN. DMF, acetonitrile, and dichloromethane were distilled from phosphorus pentoxide, while benzene was distilled from sodium prior to use. All other reagents were used without further purification.

2.1.1. [Fe (sal$_2$-trien)] [Au(dcbdt)$_2$] (1)

A solution of [Fe(sal$_2$-trien)] (PF_6) (17.00 mg, 3.06×10^{-2} mmol) in 20 mL of acetonitrile was added dropwise to a solution of (n-Bu_4N) [Au(dcbdt)$_2$] (20.40 mg, 2.49×10^{-2} mmol), in the same amount of the same solvent. Slow evaporation under nitrogen flow gave 19.41 mg of black parallelepipedic crystals, which were washed with cold acetonitrile. Yield: 80%, m.p. 277 °C (dec.). *Anal.* Calc. for $C_{36}H_{24}AuFeN_8O_2S_4$ **1**: C, 43.87; H, 2.86; N, 11.37; S, 13.01. Found: C, 43.32; H, 3.15; N, 11.17; S, 11.47%. IR (KBr, cm^{-1}) $\upsilon = 3267$ (N–H, w) 2219 (C≡N, s), 1640(C=N, s), 530(Fe–N, w), 440(Fe–O, w), 400(Fe–O, w), 350 (Au–S, w).

2.1.2. [Fe(sal$_2$-trien)] [Ni(dcbdt)$_2$] (2)

A similar procedure as used for **1** was followed and 19.97 mg of black parallelepipedic crystals were obtained. Yield: 82%. *Anal.* Calc. for $C_{35}H_{24}NiFeN_8O_2S_4$ **2**: C, 51.27; H, 2.87; N, 13.29; S, 15.21. Found: C, 51.10; H, 2.51; N, 13.17; S, 15.27%.

2.1.3. [Fe(phen)$_3$] [Au(dcbdt)$_2$]$_2 \cdot CH_3CN$ (3)

A solution of [Fe(phen)$_3$] (PF_6)$_2$ (30.00 mg, 0.05 mmol) in 25 mL of acetonitrile was added dropwise to a solution of (n-Bu_4N) [Au(dcbdt)$_2$] (45.00 mg, 0.04 mmol), in the same amount of the same solvent. Slow evaporation gave

Table 1
Crystallographic data and refinement details for compounds **2**, **3** and **4**

	[Fe(sal$_2$-trien)] [Ni(dcbdt)$_2$] (**2**)	[Fe(phen)$_3$] [Au(dcbdt)$_2$]$_2$ (**3**)	[Fe(phen)$_3$] [Ni(dcbdt)$_2$]$_2$ (**4**)
Empirical formula	$C_{36}H_{28}N_8O_2S_4FeNi$	$C_{70}H_{35}Au_2FeN_{15}S_8$	$C_{70}H_{35}FeN_{15}Ni_2S_8$
Formula weight	847.46	1792.39	1515.88
Temperature (K)	294(2)	150(2)	110(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system, specific gravity	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$
a (Å)	7.9258(3)	9.4912(7)	9.3961(9)
b (Å)	14.5604(6)	12.2375(9)	12.1885(14)
c (Å)	17.042(7)	27.525(2)	27.565(3)
α (°)	76.5370(10)	83.263(5)	83.575(7)
β (°)	76.0450(10)	89.455(5)	89.588(7)
γ (°)	75.4980(10)	87.806(5)	88.038(7)
Volume (Å^3)	1816.5(8)	3172.5(4)	3135.2(6)
Z, D_{calc} (g/cm^{-3})	2, 1.549	2, 1.876	2, 1.606
M (mm^{-1})	1.194	5.161	1.149
F(000)	868	1744	1540
Crystal size (mm)	$0.30 \times 0.16 \times 0.06$	$0.20 \times 0.02 \times 0.01$	$0.14 \times 0.08 \times 0.04$
θ Range (°)	2.94–26.37	2.27–26.46	2.63–25.68
Limiting indices hkl	−6/9, −17/18, −21/21	−11/11, −15/15, −34/34	−11/11, −14/14, −33/33
Reflections collected	29801	48921	51740
Independent reflections [R_{int}]	7377 [0.0602]	12959 [0.0943]	11895 [0.0903]
$T_{max,\ min}$	0.9318, 0.7159	0.9502, 0.4250	0.9555, 0.8557
Data/restraints/parameters	7377/0/479	12959/0/866	11895/0/866
S on F^2	0.971	0.939	1.044
R ($I > 2\sigma$(I))	$R_1 = 0.0451$, w$R = 0.0965$	$R_1 = 0.0406$, $wR = 0.0666$	$R_1 = 0.0526$, $wR = 0.1051$
R (all data)	$R_1 = 0.0839$, $wR = 0.1074$	$R_1 = 0.0856$, $wR = 0.0740$	$R_1 = 0.0962$, $wR = 0.1164$
$\Delta_{max,\ min}$ (e Å^{-3})	0.469, −0.337	1.065, −0.908	2.469, −1.938